Year: 2006

cis-(6RS,13RS)-3,3,10,10-Tetramethyl-6,13-diphenyl-1,8-dioxa-4,11-diazacyclotetradecane-2,5,9,12-tetraone and two of its precursors

Linden, Anthony ; Iliev, B ; Heimgartner, H

Abstract: The title macrocycle, C26H30N2O6, (VI), was obtained by ;direct amide cyclization' from the linear precursor 3-hydroxy-N-[1-methyl-1-(N-methyl-N-phenylcarbamoyl)ethyl]-2-phenylpropanamide, the N-methylanilide of rac-2-methyl-2-[(3-hydroxy-2-phenylpropanoyl)amino]propanoic acid, C13H17NO4, (IV). The reaction proceeds via the intermediate rac-2-(2-hydroxy-1-phenylethyl)-4,4-dimethyl-1,3-oxazol-5(4H)-one, C13H15NO3, (V), which was synthesized independently and whose structure was also established. Unlike all previously described analogues, the title macrocycle has the cis-diphenyl configuration. The 14-membered ring has a distorted rectangular diamond-based [3434] configuration and intermolecular N-H...O hydrogen bonds link the molecules into a three-dimensional framework. The propanoic acid precursor forms a complex series of intermolecular hydrogen bonds, each of which involves pairwise association of molecules and which together result in the formation of extended two-dimensional sheets. The oxazole intermediate forms centrosymmetric hydrogen-bonded dimers in the solid state.

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cis-(6*RS*,13*RS*)-3,3,10,10-Tetramethyl-6,13-diphenyl-1,8-dioxa-4,11-diaza-cyclotetradecane-2,5,9,12-tetraone and two of its precursors

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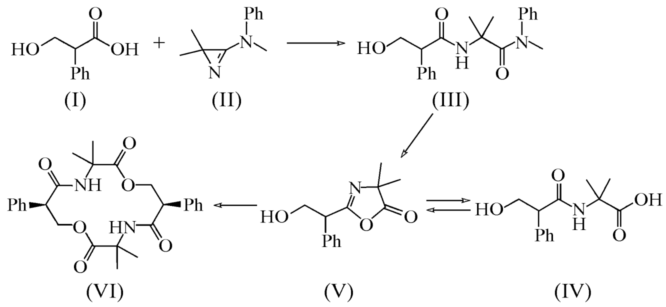
The title macrocycle, $C_{26}H_{30}N_2O_6$, (VI), was obtained by 'direct amide cyclization' from the linear precursor 3-hydroxy-*N*-[1-methyl-1-(*N*-methyl-*N*-phenylcarbamoyl)ethyl]-2-phenyl-propanamide, the *N*-methylanilide of *rac*-2-methyl-2-[(3-hydroxy-2-phenylpropanoyl)amino]propanoic acid, $C_{13}H_{17}NO_4$, (IV). The reaction proceeds *via* the intermediate *rac*-2-(2-hydroxy-1-phenylethyl)-4,4-dimethyl-1,3-oxazol-5(4*H*)-one, $C_{13}H_{15}NO_3$, (V), which was synthesized independently and whose structure was also established. Unlike all previously described analogues, the title macrocycle has the *cis*-diphenyl configuration. The 14-membered ring has a distorted rect-angular diamond-based [3434] configuration and inter-molecular N—H⋯O hydrogen bonds link the molecules into a three-dimensional framework. The propanoic acid precursor forms a complex series of intermolecular hydrogen bonds, each of which involves pairwise association of molecules and which together result in the formation of extended two-dimensional sheets. The oxazole intermediate forms centrosymmetric hydrogen-bonded dimers in the solid state.

Comment

Cyclic depsipeptides are renowned for their biological activity, mainly as antibiotics, due to their ability to allow cations selectively to pass through the cell membrane (Ballard *et al.*, 2002). A useful method for the synthesis of some analogues, which contain α,α-disubstituted α-amino acids, from linear precursors is the so-called 'direct amide cyclization' (Obrecht & Heimgartner, 1984, 1987). The starting materials for the cyclization are hydroxy oligoamides, such as compound (III) (see scheme), which possess one or several α,α-disubstituted α-amino acids and which are conveniently accessible from the corresponding hydroxy acids [*e.g.* (I)] and 2*H*-azirin-3-amines [*e.g.* (II)] *via* the 'azirine/oxazolone method' (Wipf & Heim-gartner, 1990; Heimgartner, 1991). Treatment of the hydroxy oligoamides with HCl gas in toluene at 373 K yields nine- to 24-membered cyclic depsipeptides in good yields *via* the formation of 1,3-oxazol-5(4*H*)-ones as intermediates (Obrecht & Heimgartner, 1987; Koch *et al.*, 2000, 2001; Köttgen *et al.*, 2006).



Our recent studies have shown that, when β-hydroxy acid amides analogous to compound (III) are used, 14-membered cyclodepsipeptides were formed instead of the expected seven-membered monomers. Again, the corresponding 1,3-oxazol-5(4*H*)-ones were shown to be intermediates (Iliev *et al.*, 2003, 2006). Furthermore, in comparable experiments with racemic starting materials, the cyclodimers obtained were *trans*-configured and no *cis* isomers could be detected. Other cyclization methods that started from hydroxy acids [*e.g.* (IV)], which were derived from α,α-disubstituted analogues of compound (III), gave the same result (Iliev *et al.*, 2003, 2006). Further studies showed that, in order for the reactions to have a practical value, it is a requirement that the β-hydroxy acid is α,α-disubstituted. When that was not the case, water elim-ination occurred and no cyclic products could be isolated, although the intermediate oxazolone, like compound (V), could be detected by means of IR spectroscopy and its presence proven chemically (Iliev *et al.*, 2006). Only in a single case, when the starting β-hydroxy acid amide, (III), contained the α-phenyl-β-hydroxy acid moiety, could crystals of a 14-membered cyclodepsipeptide be isolated, namely the title compound, (VI). The hydroxy acid, (IV), was obtained after selective hydrolysis of (III) by treatment with 3 *N* HCl in tetrahydrofuran. The intermediate oxazolone, (V), could be isolated after treatment of (IV) with *N*,*N*′-dicyclohexyl-carbodiimide in ethyl acetate. As part of the full character-ization of the reaction products shown in the scheme and in order to confirm the stereochemistry of compound (VI), the crystal structures of compounds (IV), (V) and (VI) were determined and are described here.

Compound (IV) crystallizes in a centrosymmetric space group and is therefore a racemate: the selected reference molecule has the *R* configuration at C5 (Fig. 1). The geometric parameters involving the non-H atoms are within normal ranges. The molecule possesses three hydrogen-bond donors, which are all involved in intermolecular interactions (Table 1). These interactions combine to link the molecules into extended two-dimensional sheets which lie parallel to the (001) plane (Fig. 2). Within the sheets, several hydrogen-bonding motifs (Bernstein *et al.*, 1995) can be discerned. The carboxylic acid H atom interacts with the carbonyl O atom of the carboxylic acid group of a neighbouring molecule, which, in turn, acts as a donor for an identical interaction back to the original molecule. These interactions result in pairs of molecules being linked into dimers across crystallographic centres of inversion. This pattern can be described by a graph-set motif of $R_2^2(8)$, which is one of the classic motifs found in the crystal structures of carboxylic acids. The H atom of the hydroxy group forms an intermolecular hydrogen bond with the amide O atom of a different neighbouring molecule. Again, this interaction links pairs of molecules into centrosymmetric dimers and the pattern can be described by a graph-set motif of $R_2^2(12)$. In a similar fashion, the amide H atom forms an intermolecular hydrogen bond with the hydroxy O atom of a third neighbouring molecule. This interaction also links pairs of molecules into centrosymmetric dimers with the $R_2^2(12)$ motif. The interactions involving the H atoms of the hydroxy and amide groups can also be combined in an alternating fashion to yield extended co-operative $\cdots$O—H$\cdots$O═C—N—H$\cdots$O—H$\cdots$ chains, which run parallel to the [100] direction and can be described by a binary graph-set motif of $C_2^2(6)$.

Free refinement of the carboxylic acid H atom in (IV) resulted in a rather long O2—H2 distance, while the associated hydrogen-bonding H$\cdots$O and O$\cdots$O distances in the $R_2^2(8)$ motif between the opposing carboxylic acid functions in two adjacent molecules are quite short (Table 2). This indicates that the pairwise intermolecular hydrogen-bonding interactions are quite strong. In such cases, some practitioners have described observations that suggest there may be a tendency for the hydrogen bonds to become more symmetrical, disordered across the O$\cdots$O vector, or even perfectly symmetrical (Gilli *et al.*, 1994; Alfonso *et al.*, 2001). The refined position of atom H2, at first glance, seems to support the idea of partial symmetricalization of the H-atom position, but other evidence suggests that the refined position may be misleading. Firstly, the refined isotropic atomic displacement parameter of atom H2 is somewhat larger than normal and larger than those of the hydroxy and amide H atoms, whose positions and atomic displacement parameters were also refined. Secondly, a contoured difference Fourier map produced by *PLATON* (Spek, 2003), in which the site-occupation factor of atom H2 had been set to 0.001, clearly shows that the electron density does indeed extend a low ridge towards the acceptor O atom, but that the maximum of the electron density is quite clearly defined and is located closer to atom O2 than the refined position of atom H2 (Fig. 3). The maximum is estimated to be

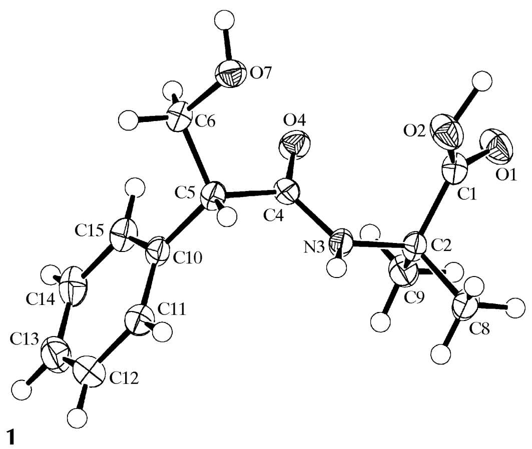


Figure 1
A view of the *R* enantiomer in racemic (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

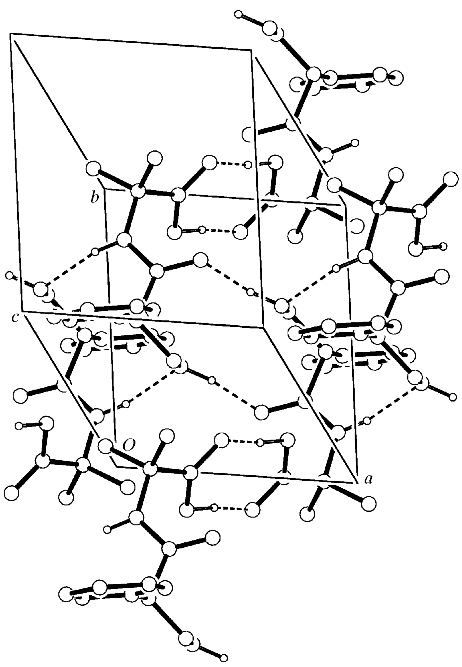


Figure 2
A hydrogen-bonded sheet in (IV). The hydrogen bonds are shown by dashed lines and the $R_2^2(8)$, two $R_2^2(12)$ and $C_2^2(6)$ motifs are clearly visible.

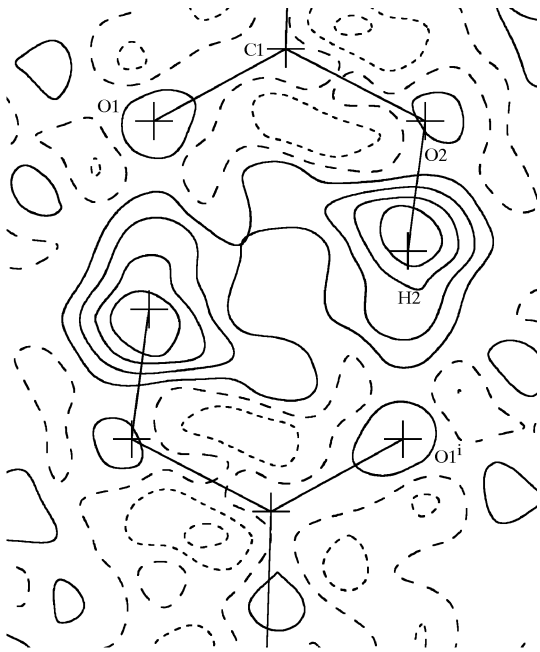


Figure 3
A contoured difference Fourier map slice in the plane of the carboxylic acid group of (IV), with the site-occupancy factor of atom H2 set to 0.001. The refined positions of the atoms are shown by + marks. The contour intervals are 0.1 e Å^{-3}. [Symmetry code: (i) $-x+1, -y+2, -z$.]

about 0.83 Å from atom O2, which is surprisingly close to the normally expected O—H distance of 0.84 Å at the temperature of the measurement (160 K). This result suggests that the refined position of atom H2 does not necessarily truly represent the majority of the electron-density distribution in this case and that there may be little, if any, symmetricalization of the hydrogen bond. The result further shows the importance of examining contoured difference Fourier maps whenever potentially unusual H-atom positions are being investigated.

Compound (V) also crystallized as a racemate and again the reference molecule was selected as having the *R* configuration (Fig. 4). The oxazole ring is planar, with this plane making an angle of 87.02 (6)° with the plane of the phenyl ring. The hydroxy H atom forms an intermolecular hydrogen bond with the N atom of the oxazole ring of a neighbouring molecule which, in turn, acts as a donor for an identical interaction back to the original molecule (Table 2). These interactions link centrosymmetrically related pairs of molecules into dimers and can be described by a graph-set motif of $R_2^2(12)$.

Compound (VI) crystallized as a racemate, albeit in a non-centrosymmetric space group. The compound has the 6*RS*,13*RS* configuration, which means that the phenyl substituents have a *cis* relationship: the selected reference molecule has a 6*R*,13*R* configuration (Fig. 5). The *cis* orientation of the phenyl groups was unexpected, as all previous analogous reactions starting from racemic materials had yielded *trans*-configured cyclodimers (Iliev *et al.*, 2003, 2006). The 14-membered ring conformation, while corrugated, is not folded. When viewed perpendicular to the mean ring plane, the ring appears to have a distorted variant of the rectangular diamond-lattice [3434] conformation often observed for this size of organic macrocycle (Groth, 1979; Chan *et al.*, 1985) and predicted to be slightly more stable than the [3344] and [3335] conformations (Dale, 1973). The lactone and lactam groups sit along the '3' and '4' sides of the rectangle, respectively, while the phenyl and methyl substituents occur at the corners. The torsion angles along the sides of the rectangle (Table 3) are close to the ideal value of 180°, with the greatest deviation of about 6° being observed within the lactam groups. The corners of an ideal [3434] rectangle are characterized by two consecutive torsion angles of the same sign and values of ±60°, and it is here that the ring in (VI) shows the greatest deviation from ideality. The dimethyl-substituted corners have a sharper turn, as demonstrated by both torsion angles being up to 17° less than 60°. The phenyl-substituted corners are completely outside the expected pattern, with one torsion angle having a magnitude of about 127° and the following torsion angle being opposite in sign and with a magnitude of about 64°. The five-atom and four-atom planes formed by the lactone and lactam sides of the rectangle, respectively, are reasonably planar, with the maximum deviations in each type of plane being 0.023 (2) and 0.042 (3) Å, respectively. The greater deviation from planarity of the sides containing the lactam groups is in keeping with the greater deviation of the lactam torsion angle from 180°. Most significantly, instead of the planes of opposing flanks being parallel, as in the ideal diamond-based conformation, the planes of the two lactam sides intersect at an angle of 24.4 (4)°, while those of the two lactone sides intersect at an angle of 80.6 (4)°, which means that the lactone carbonyl groups are turned well away from one another. The described distortions may all be a consequence of twists in the macrocyclic ring conformation, induced by the *cis*-positioned phenyl substituents preferring to occupy equatorial positions. The phenyl ring planes are approximately perpendicular to the mean plane of the macrocyclic ring. One of the phenyl rings is disordered with an approximately 2:1 ratio of orientations, and the two orientations differ by a twist of 22.0 (1)° about the C17···C20 axis.

The lactam groups in the molecules of (VI) are oriented such that their donor H atoms point towards the same side of the macrocyclic ring and, in addition, the molecules pack such that all of the N—H bonds in the structure face in roughly the same direction. The crystallographic *c*-glide plane does not flip any molecules up the other way, as it lies approximately perpendicular to the mean plane of the macrocyclic ring. In the structures of the previously examined analogues (Iliev *et*

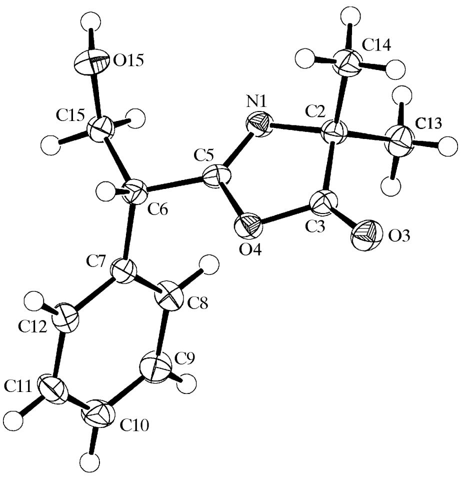


Figure 4
A view of the *R* enantiomer in racemic (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

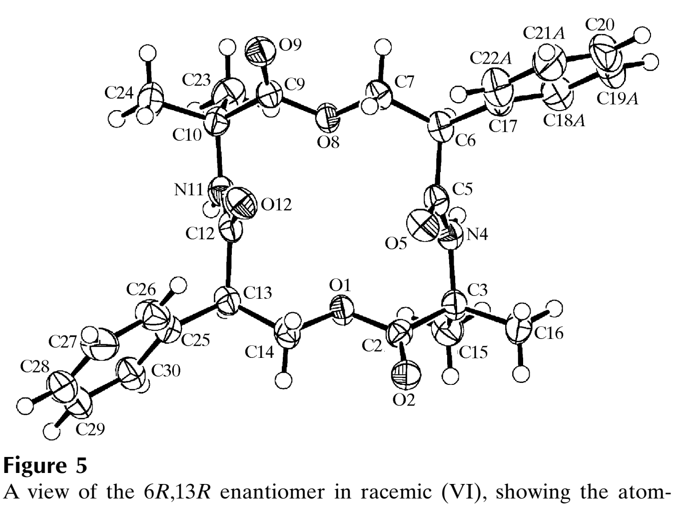


Figure 5
A view of the 6*R*,13*R* enantiomer in racemic (VI), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Only the major conformation of the disordered phenyl ring is shown.

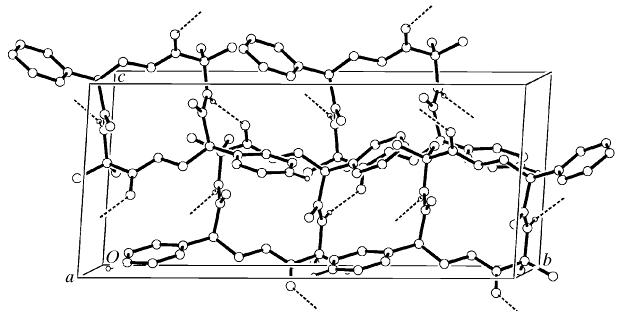


Figure 6
The crystal packing in (VI), showing the intermolecular hydrogen bonds as dashed lines.

al., 2003, 2006), the centrosymmetric nature of the molecules meant that the amide H atoms pointed to opposite sides of the macrocyclic ring. This difference has consequences for the hydrogen-bonding pattern. In the previous structures, hydrogen bonds formed between the lactam N—H groups and the lactone O atoms of neighbouring molecules and assembled the centrosymmetric molecules into stacks of ladder-like columns, where the macrocycle acted as the ladder rung and the hydrogen bonds were the rung supports, with the directional sense of the support (the N—H → O direction) on opposing sides of a rung being opposite. In (VI), the lactam N—H groups also form intermolecular hydrogen bonds with the lactone O atoms of neighbouring molecules (Table 4), but instead of a ladder-like arrangement, the hydrogen bonds link to diagonally offset neighbouring molecules, with each of the two symmetry-independent interactions going off in different directions (Fig. 6). Taken individually, the interactions link the molecules into extended chains, each of which has a graph-set motif of $C(5)$. The chains involving N4—H and N11—H run in the [101] and [001] directions, respectively. In essence, each molecule donates hydrogen bonds to two neighbouring molecules and accepts two hydrogen bonds from two other molecules, so that, taken together, these interactions serve to link the molecules into an extended three-dimensional framework.

Experimental

Compound (III) was prepared in 88% yield by the reaction of DL-tropic acid, (I) (332 mg, 2 mmol), and 2,2,*N*-trimethyl-*N*-phenyl-2*H*-azirin-3-amine, (II) (370 mg, 2.11 mmol), in tetrahydrofuran (20 ml) at room temperature, according to a known protocol (Obrecht & Heimgartner, 1987). Hydroxy acid (IV) was obtained by treatment of (III) (340 mg, 1 mmol) with a 3 *N* solution of HCl in tetrahydrofuran (3 ml) for 4 h at room temperature and subsequent extraction with ethyl acetate. Suitable crystals of (IV) were obtained by slow recrystallization from a mixture of dichloromethane–2-propanol–hexane (m.p. 498–501 K). The treatment of (IV) (126 mg, 0.5 mmol) with *N*,*N*′-dicyclohexylcarbodiimide (104 mg, 0.5 mmol) in ethyl acetate (10 ml) overnight at room temperature, followed by filtration, washing with ethyl acetate and recrystallization of the residue from acetonitrile, yielded 93 mg (79%) of (V) (m.p. 392–395 K). The treatment of (IV) (126 mg, 0.5 mmol) with Bu_2SnO (50 mg) in xylene (150 ml) under reflux for 2 d (Iliev *et al.*, 2003), followed by evaporation of the solvent, washing with diethyl ether and recrystallization from acetone–hexane–2-propanol, yielded 9 mg (5%) of (VI) as colourless crystals. The same compound was isolated in small amounts by treatment of (III) (170 mg, 0.5 mmol) in toluene (100 ml) at 373 K with HCl (gas) for 8 min, followed by chromatographic purification (silica gel, dichloromethane–acetone 20:1).

Compound (IV)

Crystal data

$C_{13}H_{17}NO_4$
$M_r = 251.28$
Triclinic, $P\overline{1}$
$a = 6.6567$ (2) Å
$b = 9.1317$ (3) Å
$c = 10.8486$ (3) Å
$\alpha = 99.2298$ (16)°
$\beta = 98.278$ (2)°
$\gamma = 99.5405$ (19)°
$V = 631.98$ (3) Å^3
$Z = 2$
$D_x = 1.320$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 160$ (1) K
Tablet, colourless
0.25 × 0.17 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
15315 measured reflections
2900 independent reflections
2129 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.139$
$S = 1.06$
2898 reflections
178 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 + 0.1385P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.067 (12)

Table 1
Hydrogen-bond geometry (Å, °) for (IV).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯O1^{i}	1.08 (3)	1.55 (4)	2.6307 (16)	174 (3)
O7—H7⋯O4^{ii}	0.95 (3)	1.74 (3)	2.6780 (16)	167 (2)
N3—H3⋯O7^{iii}	0.89 (2)	1.98 (2)	2.8523 (18)	166 (2)

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+1, -y+1, -z$; (iii) $-x, -y+1, -z$.

Compound (V)

Crystal data

$C_{13}H_{15}NO_3$
$M_r = 233.27$
Monoclinic, $P2_1/c$
$a = 10.1934$ (2) Å
$b = 9.9466$ (2) Å
$c = 11.9331$ (3) Å
$\beta = 103.3915$ (9)°
$V = 1177.00$ (4) Å^3
$Z = 4$
$D_x = 1.316$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 160$ (1) K
Prism, colourless
0.35 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans with κ offsets
28758 measured reflections
3422 independent reflections
2638 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 30.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.108$
$S = 1.04$
3421 reflections
161 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.2303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.020 (4)

Table 2
Hydrogen-bond geometry (Å, °) for (V).

D—H···A	D—H	H···A	D···A	D—H···A
O15—H15···N1^{i}	0.915 (19)	1.92 (2)	2.8316 (12)	174.8 (16)

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Compound (VI)

Crystal data

$C_{26}H_{30}N_2O_6$	$Z = 4$
$M_r = 466.53$	$D_x = 1.228$ Mg m^{-3}
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 15.9437$ (2) Å	$\mu = 0.09$ mm^{-1}
$b = 19.1979$ (4) Å	$T = 160$ (1) K
$c = 11.2587$ (2) Å	Prism, colourless
$\beta = 132.9182$ (7)°	0.15 × 0.15 × 0.10 mm
$V = 2523.69$ (8) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	2217 independent reflections
ω scans with κ offsets	1883 reflections with $I > 2\sigma(I)$
16028 measured reflections	$R_{int} = 0.058$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.2754P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.097$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.22$ e Å^{-3}
2215 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
357 parameters	Extinction correction: *SHELXL97*
H atoms: see below	Extinction coefficient: 0.0056 (10)

Table 3
Selected torsion angles (°) for (VI).

O1—C2—C3—N4	51.6 (3)	O8—C9—C10—N11	48.8 (3)
C2—C3—N4—C5	42.9 (4)	C9—C10—N11—C12	44.2 (3)
C3—N4—C5—C6	173.7 (2)	C10—N11—C12—C13	173.8 (3)
N4—C5—C6—C7	126.5 (3)	N11—C12—C13—C14	127.6 (3)
C5—C6—C7—O8	−63.0 (3)	C12—C13—C14—O1	−64.5 (3)
C6—C7—O8—C9	179.9 (2)	C13—C14—O1—C2	179.3 (2)
C7—O8—C9—C10	−178.2 (2)	C14—O1—C2—C3	−177.6 (2)

Table 4
Hydrogen-bond geometry (Å, °) for (VI).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O2^{i}	0.80 (3)	2.37 (3)	3.138 (3)	160 (3)
N11—H11···O9^{ii}	0.85 (4)	2.16 (4)	2.983 (4)	161 (3)

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x, -y+2, z+\frac{1}{2}$.

In the structure of compound (VI), one of the phenyl rings is disordered over two orientations which result from a pivot about the C17···C20 axis of the ring. Two positions were defined for each of the other four atoms of this ring and refinement of constrained site-occupation factors for the two orientations yielded a value of 0.67 (3) for the major conformation. All C—C bond lengths within both orientations of the disordered ring were restrained to be similar, while neighbouring atoms within and between each conformation of the disordered ring were restrained to have similar atomic displacement parameters. Compound (VI) crystallized in a non-centrosymmetric space group with a polar axis, but the presence of glide planes indicates that the compound in the crystal is racemic. In the absence of significant anomalous dispersion effects, Friedel opposites were merged prior to the final cycles of refinement and the absolute structure was assigned arbitrarily. The amide, hydroxy and carboxylic acid H atoms of (IV), the hydroxy H atom of (V) and the amide H atoms of (VI) were placed in the positions indicated by difference electron-density maps and their positions were allowed to refine together with individual isotropic displacement parameters. In each structure, the methyl H atoms were constrained to an ideal geometry [C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$], but were allowed to rotate freely about the C—C bonds. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atom at distances of 0.95, 0.99 or 1.00 Å for phenyl, methylene or methine groups, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$. For (IV), (V) and (VI), two, one and four low-angle reflections, respectively, were omitted from the final cycles of refinement because their observed intensities were much lower than the calculated values as a result of being partially obscured by the beam stop.

For all compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); structure solution: *SIR92* (Altomare *et al.*, 1994); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3017). Services for accessing these data are described at the back of the journal.

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